More Happy, Less Stable: Surface Complexions in Lithium Thiophosphates

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Lithium thiophosphates (LPS) based solid electrolytes are among the most promising materials for next-generation all-solid-state lithium ion batteries due to their high ionic conductivity. However, their practical deployment is hindered by surface-driven degradation processes, including reactions with moisture, solvents, and electrode materials. A detailed atomistic understanding of LPS surfaces remains challenging because of their structural complexity and lacking experimental characterization.

Here, we employ machine-learning interatomic potentials to investigate the structure, properties, and dynamics of β-Li_3PS_4 surfaces across extended spatial and temporal scales inaccessible to conventional first-principles simulations. Molecular dynamics simulations reveal surface complexions that emerge through spontaneous surface reconstruction. These complexions exhibit characteristics distinctly different from the crystalline bulk, including local amorphization, densification, modified lithium transport pathways, and altered electronic environments.

To characterize the stability and dynamics of the reconstructed surfaces, we introduce physically motivated structural descriptors that capture the evolving ensemble of surface states and reveal the strongly dynamic nature of the electrolyte surface. Insights on the electronic structure and reactivity with water reveals higher thermodynamic driving forces after reconstruction, providing a new understanding of surface reactivity and degradation processes in sulfide solid electrolytes [1].

The results open the pathway for targeted data-driven interfacial engineering aimed to passivate reactive surface complexions, suppress degradation pathways, and enhance the environmental and electrochemical stability of sulfide electrolytes. Together with an experimental collaboration, we use these insights to explore surface coatings and to establish design principles for controlling interfacial chemistry in sulfide electrolytes. Our results demonstrate how machine-learning atomistic models can bridge the gap between atomistic simulations and realistic operating conditions, enabling the discovery and characterization of complex surface phenomena and systematic property design in energy materials.

References

[1] H. Türk, D. Tisi, and M. Ceriotti, *PRX Energy* **4**, 033010 (2025).